Using Quantum Mechanics to Predict Shock Properties of Explosives

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ABSTRACT

The almost exponential increase in computer power over the last few decades has opened up the venue for increasingly more advanced and accurate computer simulations. As little as ten years ago, quantum mechanical calculations were restricted to predictions of static properties of systems containing tens of atoms, thus limiting first principles explorations to gas phase chemical and physical processes. With today's computers, quantum mechanical calculations can easily be performed for solids and liquids, thus opening up exploration into condensed phase physico-chemical processes. In this work, we demonstrate the ability of quantum mechanical approaches, in particular the density-functional method, to predict shock properties of condensed phase energetic materials.

1. INTRODUCTION

With the emergence of teraflop supercomputing, the inclusion of atomistic simulation methods in critical energetic materials (EM) research and development programs supporting Future Force weaponry has become a reality. Modeling using atomistic methods provides detailed information about the fundamental chemical and physical processes that control the conversion of an energetic material to products, thus providing the designer with information with which he can tailor a material for specific performance. Such predictive capabilities also allow for screening of notional materials upon conception, allowing for elimination of poor candidates before investing in synthesis and testing. At this time, the most popular atomistic simulation method is that of classical molecular dynamics (CMD), which involves integrating the classical equations of motion to generate temporal profiles of atomic positions and velocities, thus providing a dynamic description of the system. Also, thermodynamic information can be obtained by averaging properties evaluated at each integration step over the duration of the simulation.

The most significant limitation of a CMD simulation is its dependence on a model description of the interactions among all particles in the system. Typically, the models are empirical potentials fitted using experimental information and available quantum mechanical (QM) results. If the function accurately describes the region of phase space to be sampled during the CMD simulation, then the results will be quite reliable; if not, then the results cannot be assumed to be predictive. It is virtually impossible to accurately parameterize empirical potentials to describe interatomic interactions at all conditions of interest. In fact, there are no CMD models available that accurately predict chemical and physical properties of EMs under all conditions. Therefore, we are currently faced with either enhancing existing imperfect empirical models of EMs (by making them system-specific and thus not necessarily transferable to other systems) or using first-principles QM methods which are, by their nature, transferable. Since the latter is obviously more desirable, we have directed a great deal of effort toward integrating QM predictions of static and dynamic properties of EMs into our suite of modeling capabilities.

To demonstrate this advanced modeling capability in an EM application, we present the first QM calculation of the shock Hugoniot of an explosive. The Hugoniot curve, which characterizes a shocked material, can be used in the design of new materials or weaponry. The system we have chosen is nitromethane, a prototypical energetic material for which numerous experimental data are available, including that of the shock Hugoniot. Additionally, thermochemical and CMD predictions of the shock Hugoniot using empirical methods are available for comparison.

CMD calculations of the shock Hugoniot of nitromethane have been performed using an empirical interatomic interaction potential developed by Sorescu et al. (1999); however, this same model fails to predict properties of certain EMs under conditions of extreme compression (Sorescu et al., 2000). In sharp contrast, the more accurate and transferable QM methods, in particular density functional theory (DFT) (Hohenberg and Kohn, 1964) can readily explore the extreme pressure and temperature regimes associated with detonation and is not system specific. Its main limitation is that of computational expense, which can be prohibitive for large systems. To present date the only other materials whose shock Hugoniot has been computed by DFT are nitrogen (Mattson 2003) and deuterium (Lenosky et al., 2000; Desjarlais, 2003; Bonev et al., 2004), neither of which are conventional explosives.

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As an exploratory study on the suitability of DFT to predict shock Hugoniots for materials of interest to the Army, we have first generated the shock Hugoniot of diamond. This system was chosen because of the availability of experimental data and theoretical models, both at the classical and quantum mechanical level. The comparison is shown in Figure 1 (experimental data is taken from Pavloskii (1971) and Kondo et al. (1983)). As evident in this figure, the empirical potential of Tersoff (1988) demonstrates unphysical behavior at relatively small degrees of compression, while DFT concretely reproduces experimental information. Thus, these calculations clearly demonstrate the superiority of DFT for use in predicting the shock Hugoniot of materials. This results presented in this study will provide motivation for future investment into development and integration of accurate quantum mechanical methods into the suite of tools for computational modeling of EMs.

Materials of interest to Future Force weapons (e.g. energetic materials, advanced armor) are destined to be subjected to extreme impacts leading to substantial physical or chemical changes in the atomic structure of the material. Molecular dynamics (MD) simulation, an atomistic simulation method that provides a temporal description of the behavior of a system subjected to initiating events, is a particularly effective means to examine complex changes occurring in condensed phase materials after shock, including reaction and failure waves, phase transitions, and defect formation and propagation. Such a detailed examination cannot be performed experimentally; however, the detailed information obtained from these simulations can easily be used to either design experiments that will transform the material to a desired state upon shock, or to design new materials with tailored shock properties.

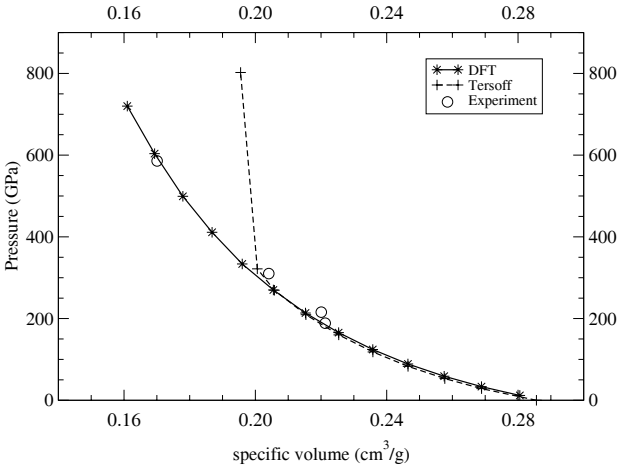

Figure 1: Comparison of the diamond shock Hugoniot between experiment, the empirical potential of Tersoff and DFT. The experimental data is from Pavloskii (1971) and Kondo et al. (1983).

2. SHOCK HUGONIOT

The equation of state (EOS) reveals the physical properties of a material given a set of thermodynamic conditions. It can be used to determine such properties as the heat capacity, bulk modulus, and thermal expansion coefficients. In general, the EOS is too complicated to be derived using statistical mechanics except for simple toy models like the ideal gas. In mose cases, the EOS is a complicated analytic model which is fit to data obtained from either experiment or theory.

Of particular interest to detonation physics, is the exploration of the EOS at extreme conditions of pressure and temperature. These extreme conditions can be experimentally achieved either under hydrostatic or shock conditions. The advent of the diamond anvil cell (DAC), has allowed experimentalists to reach pressures (up to 200 GPa) previously only obtainable by shock methods. Nevertheless, this has not decreased the necessity to study materials under shock conditions since these shock methods (e.g., gas-gun, laser-induced, or flyer-plate) are able to reach extreme pressures (> 200 GPa) and temperatures (> 4000 K) which are not unattainable without destroying the diamonds in the DAC. Furthermore, knowledge of the behavior of a material under shock conditions provides knowledge of the states in the detonation process.

The thermodynamic states accessible under shock conditions is given by the Hugoniot which is the locus of points in (E,P,V)-space satisfying the condition:

$$E_1 - E_0 = \frac{1}{2}\left(P_1 + P_0\right)\left(V_1 - V_0\right) \tag{1}$$

where E is the internal energy, P is the pressure, V is the volume and the subscripts 0 and 1 denote the initial and shocked state, respectively. This relation follows from conservation of matter, momentum, and energy for an isolated system compressed by a pusher at a constant velocity. In the canonical (NVT) ensemble, it is often convenient to define the Hugoniot function (Erpenbeck, 1992; Rice et al., 1996)

$$\begin{aligned} h\left(T,V\right) &= E(T,V) - E(T_0,V_0) \\ &- \frac{1}{2}\left[P\left(T,V\right) + P(T_0,V_0)\right]\left(V_0 - V\right) \end{aligned} \tag{2}$$

The locus of states which satisfy $h(T_h,V_h) = 0$ is the principal Hugoniot. Since one does not know the points in phase space which satisfy the principle Hugoniot

condition a priori, it is almost always necessary to interpolate using neighboring points

3. COMPUTATIONAL METHOD

The principal Hugoniot conditions are determined using a method proposed by Erpenbeck (1992). In this method, EOS points over a range of T, V and P are generated using molecular dynamics. In this work, we will use canonical molecular dynamics (NVT-MD) to evaluate all EOS points. Each principal Hugoniot point is determined through the following steps. First, after selecting a volume for which the Hugoniot point is desired, NVT-MD simulations are performed for a few temperatures believed to correspond to that for which the Hugoniot function Eq. (2) is zero. The Hugoniot function Eq. (2) is evaluated for each temperature, and this set of Hugoniot points is fitted to a linear equation in temperature. From this, it is trivial to determine the temperature for which Eq. (2) is zero (the Hugoniot temperature). Next, the pressures corresponding to the various simulations are also fitted to a linear equation in temperature. The Hugoniot pressure is determined simply by evaluating the fitted equation at the Hugoniot temperature.

The principal Hugoniot requires accurate calculation of the internal energy and pressure of a system at a given density and temperature. We choose to compute these thermodynamic quantities using Kohn-Sham (Kohn and Sham, 1965) density functional theory (DFT; Hohenberg and Kohn, 1964) as implemented in the VASP (Vienna *ab initio* simulation program; Kresse and Hafner, 1992; 1994; Kresse and Furthmüller, 1996; 1996) code developed at the Technical University of Vienna. Our thermodynamic quantities are computing by performing Born-Oppenheimer molecular dynamics (BOMD) in the canonical ensemble using a Nosé-Hoover thermostat for the ions (Nosé, 1984; 1984; Hoover, 1985). The core electrons are replaced with projector augmented wave (PAW; Kresse and Joubert, 1999) potentials. The exchange-correlation energy used the generalized gradient approximation (GGA) of Perdew-Berke-Ernzerhof (PBE; Perdew et al., 1996).

These DFT calculations have three major sources of convergence errors: energy cutoff, k-point sampling and finite-size. The VASP code expands the electronic states using a plane-wave basis. The accuracy of the electronic states is controlled by the plane-wave energy cutoff Ec. For our calculations, we set E_c = 520 eV which converges the total energy and pressure to at least 10 meV/atom and 2 kbar, respectively. The non-local projectors for the PAW potentials are evaluated in real-space and optimized by the method of Kresse (unpublished). While the non-local projectors are known to be more accurately evaluated in reciprocal-space, the real-space projectors are faster to evaluate and exhibit better scaling with system size. In order to appropriately balance accuracy with performance, we optimize the real-space projectors with a strict tolerance in order to minimize systematic errors in the total energies and pressures.

The Brillouin zone was only sampled using the Γ point. As our system is a liquid, the k-point sampling is not as critical as for a crystalline solid. All the calculations presented here are performed on a eight-molecule simple-cubic cell. We did not assess the finite-size effect errors for this calculation, however it is believed that they should only be significant near a phase transition. Extensive tests for finite-size effects would also be prohibitively computationally expensive.

The other major source of systematic error is the approximation to the exchange-correlation energy. Unlike the more advanced quantum mechanical techniques that treat the exchange-correlation energy more accurately, it remains an uncontrolled approximation in the density-functional method. Its limitations are widely known and documented (see e.g. Martin (2004) and references therein). In particular it is known to fail for vdW-bonded materials, such as most organic molecules, water, noble gases and other sparse matter. For energetic materials, it is known to underestimate equilibrate lattice constants and bulk moduli which are softer than experiment. Hence, there is the possibility an unpredictable error in the total energies and pressures at low compression ratios. At high compression ratios the errors from the vdW interaction is expected to be less important, and this is what is found in shock Hugoniot DFT calculations of liquid deuterium (Lenosky et al., 2000; Desjarlais, 2003; Bonev et al., 2004). The results presented here are for the low compression regime. This was chosen in order to compare with existing experimental data and to test DFT method in the “worst-case” scenario.

Lastly, we also point out that the electronic temperature was set equal to the ionic temperature, i.e. $T_{el} = T_{ion}$, using a Fermi-Dirac function for the occupation of the electronic states. All though there are arguments against this rational based on the fact that the DFT is a ground state theory, some recent quantum Monte Carlo results on liquid helium have suggested that the excited state are approximately correct (Militzer, unpublished). In any case, given that the gap at Γ is at least 2.0 eV (at the reference volume V_0) there would be almost no occupation of the excited states below T_{el} = 2000 K which is below the temperature range we explored in this work. The occupancy of the excited states could occur earlier if significant band gap closure was induced by either pressure or dissociation. This was not observed in our calculations.

4. RESULTS

The internal energy and pressure for a given point in phase space (T,V) was determined by a 2 ps equilibration period followed by statistically averaging their instantaneous values (E,P) during a 2 ps NVT MD simulation. Our principle Hugoniot was calculated by a linear least squares fit to $h(T,V_h)$ at a fixed Hugoniot volume V_h for three to four different temperatures. It was then a simple matter to determine T_h which satisfies $h(T_h,V_h) = 0$. Similarly, the associated Hugoniot pressure P_h was determined by a linear least square fit of $P(T,V_h)$ for the same temperature points; the Hugoniot pressures is then given by $P_h = P(T_h,V_h)$. To facilitate comparison with experiment and CMD, we chose the same thermodynamic variables for our reference state P_0,T_0,V_0 was 0.001 kbar, 0.889 cm^3/gm, and 298 K.[1] This was chosen to coincide with that used in the experiments of Delpuech and Menil (Delpuech and Menil, 1983) and data from Brennan (unpublished) which was generated with CMD using the Sorescu-Thompson-Rice (SRT; Sorescu et al., 1999) empirical potential.

Our initial molecular configuration were generated by placing eight nitromethane molecules equidistant from each other in a simple cubic cell and performing a 5 ps NVT MD simulation at a temperature of T = 1000 K to generate a liquid nitromethane. This was generated at the specific volume of 0.795 cm^3/gm. The initial molecular configuration at other specific volumes was generated by a simple rescaling of the atomic positions and lattice vectors which did not exceed 6%. The aforementioned rescaling process had the potential of exciting intramolecular modes in the nitromethane molecules. For sufficiently long simulation times, collisions among nitromethane molecules would eventually damp at these modes. However, the specific volumes and simulation times considered here did not meet this criteria. There is the possibility that this introduced an unwanted bias in our thermodynamic variables, particularly the pressure. This point is the subject of further investigation.

Figure 2 presents our shock Hugoniot nitromethane results. They are in reasonable agreement with experiment and the SRT data given the various sources of systematic errors in our DFT calculation in particular the lack of vdW interactions. The agreement is expected to improve at higher compression ratios where the contribution to the internal energy and pressure from the vdW interaction is less significant.

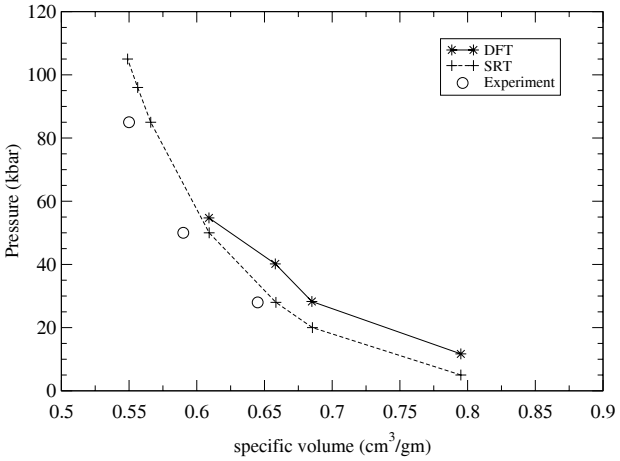

Figure 2: Comparison of nitromethane Hugoniot among experiment, the empirical potential of SRT and DFT. The experimental data is from Delpuech and Menil (1983) The CMD calculation using the SRT empirical potential was from Brennan (unpublished).

CONCLUSIONS

We have presented the *first* QM calculation of the shock Hugoniot for a conventional explosive using the first-principles DFT method. These results are encouraging in spite of the shortcomings of DFT for these class of materials which are dominated by the vdW interaction at low densities. The agreement with experiment and CMD were reasonable and no significant differences were found for the limited compression ratios reported here. Additional, Hugoniot data points are forth coming.

It is important to point out that although the empirical SRT potential gave similar results to those obtained with DFT, the latter required no ad-hoc parametrization of the fundamental interactions. The former, on the other hand, requires substantial effort, a large degree of empiricism, and still the model does not allow for simulation of complex behavior such as chemical reactivity. This makes DFT a robust and preferred method for predicting materials properties over a wide-range of thermodynamic materials for many elements on the periodic table. Additionally, because the DFT method is quantum mechanical in nature, there are material properties which can be calculated that are completely inaccessible within the classical methods, e.g. band gap, dielectric functions, polarizability, etc..

The main limitation of the DFT approach is its significant computational cost which limits the length

[1] Although the value of P_0 exceeds the accuracy to which the pressure can be reasonably calculated within any implementation of DFT, we found that our results were insensitive to P_0 for values up to several kbar.

and times scales that can be simulated using classical methods. These are typically two to three orders of magnitude in time and system size. The restriction in length and time scales is an area that awaits significant impact from algorithmic development. However, continuing advances in algorithmic development at the ARL and other service and DOE laboratories, coupled with increasingly powerful computational platforms, provide great hope that such computational limitations will soon be eased. At that point, routine application of quantum molecular dynamics simulations of energetic materials such as those presented here will be realized, and dependence on less accurate, empirical modeling will be minimized.

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